

CASE A-22210/US/A

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

IN RE APPLICATION OF

Group Art Unit:

JEAN-PIERRE WOLF ET AL

Examiner:

APPLICATION NO: Not Yet Assigned

FILED: Concurrently Herewith

FOR: ORGANOMETALLIC

MONOACYLALKYLPHOSPHINES

Assistant Commissioner for Patents

Washington, D.C. 20231

PRELIMINARY AMENDMENT

Dear Sir:

Applicants present the instant Preliminary Amendment for entry and consideration in order to place the instant continuation application in better condition for examination on its merits and for allowance.

The Commissioner is authorized to charge any fee due, or credit any overcharge, as a result of this Preliminary Amendment to Deposit Account No. 03-1935.

Please amend the above-identified patent application, without prejudice, as follows:
IN THE SPECIFICATION:

IN THE CLAIMS:

Amend claims 6 and 12 as follows:

6. (amended) A method for the preparation of mono- or bisacylphosphines, mono- or bisacylphosphine oxides or mono- or bisacylphosphine sulfides comprising reacting a compound of formula I according to claim 1.

12. (amended) A photocurable composition comprising

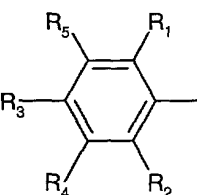
(a) at least one ethylenically unsaturated photopolymerizable compound and

(b) at least one compound of the formula II according to claim 2 or at least one compound

according to formula III
$$\text{Ar}-\overset{\overset{\text{O}}{\parallel}}{\text{C}}-\overset{\overset{(\text{A})_x}{\parallel}}{\underset{\underset{\text{R}_6}{|}}{\text{P}}}-\text{Z}_1 \quad (\text{III}), \text{ in which}$$

A is O or S;

x is 0 or 1;

Ar is a group ; or Ar is cyclopentyl, cyclohexyl, naphthyl, anthracyl,

biphenyl or an O-, S- or N-containing 5- or 6-membered heterocyclic ring, where the radicals cyclopentyl, cyclohexyl, naphthyl, anthracyl, biphenyl and 5- or 6-membered heterocyclic ring are unsubstituted or substituted by halogen, C₁-C₄alkyl and/or C₁-C₄alkoxy;

R₁ and R₂ independently of one another are C₁-C₂₀alkyl, OR₁₁, CF₃ or halogen;

R₃, R₄ and R₅ independently of one another are hydrogen, C₁-C₂₀alkyl, OR₁₁ or halogen;

or in each case two of the radicals R₁, R₂, R₃, R₄ and R₅ together form C₁-C₂₀alkylene which can be interrupted by O, S or -NR₁₄;

R_6 is C_1 - C_{24} alkyl, unsubstituted or substituted by C_5 - C_{24} cycloalkenyl, phenyl, CN, $C(O)R_{11}$, $C(O)OR_{11}$, $C(O)N(R_{14})_2$, $OC(O)R_{11}$, $OC(O)OR_{11}$, $N(R_{14})C(O)N(R_{14})$, $OC(O)NR_{14}$, $N(R_{14})C(O)OR_{11}$, cycloalkyl, halogen, OR_{11} , SR_{11} , $N(R_{12})(R_{13})$ or $-\overset{\text{O}}{\underset{\text{H}}{\text{C}}}-\text{CH}_2$;

C_2 - C_{24} alkyl which is interrupted once or more than once by nonconsecutive O, S or NR_{14} and which is unsubstituted or substituted by phenyl, OR_{11} , SR_{11} , $N(R_{12})(R_{13})$, CN, $C(O)R_{11}$, $C(O)OR_{11}$, $C(O)N(R_{14})_2$ and/or $-\overset{\text{O}}{\underset{\text{H}}{\text{C}}}-\text{CH}_2$;

C_2 - C_{24} alkenyl which is uninterrupted or interrupted once or more than once by nonconsecutive O, S or NR_{14} and which is unsubstituted or substituted by OR_{11} , SR_{11} or $N(R_{12})(R_{13})$;

C_5 - C_{24} cycloalkenyl which is uninterrupted or interrupted once or more than once by nonconsecutive O, S or NR_{14} and which is unsubstituted or substituted by OR_{11} , SR_{11} or $N(R_{12})(R_{13})$;

C_7 - C_{24} arylalkyl which is unsubstituted or substituted on the aryl group by C_1 - C_{12} alkyl, C_1 - C_{12} alkoxy or halogen;

C_4 - C_{24} cycloalkyl which is uninterrupted or interrupted once or more than once by O, S and/or NR_{14} and which is unsubstituted or substituted by OR_{11} , SR_{11} or $N(R_{12})(R_{13})$; or C_8 - C_{24} arylalkyl or C_8 - C_{24} arylalkenyl;

R_{11} is H, C_1 - C_{20} alkyl, C_2 - C_{20} alkenyl, C_3 - C_8 cycloalkyl, phenyl, benzyl or C_2 - C_{20} alkyl which is interrupted once or more than once by nonconsecutive O atoms and which is unsubstituted or substituted by OH and/or SH;

R_{12} and R_{13} independently of one another are hydrogen, C_1 - C_{20} alkyl, C_3 - C_8 cycloalkyl, phenyl, benzyl or C_2 - C_{20} alkyl, which is interrupted once or more than once by O or S and which is unsubstituted or substituted by OH and/or SH; or R_{12} and R_{13} together are C_3 - C_5 alkylene which is uninterrupted or interrupted by O, S or NR_{14} ;

Z_1 is C_1 - C_{24} alkyl, which is unsubstituted or substituted once or more than once by OR_{15} , SR_{15} ,

$N(R_{16})(R_{17})$, phenyl, halogen, CN, $-N=C=A$, $-\overset{\text{O}}{\underset{\text{H}}{\text{C}}}-\text{CH}_2$, $-\overset{\text{A}}{\underset{\text{H}}{\text{C}}}=\text{R}_{18}$, $-\overset{\text{A}}{\underset{\text{H}}{\text{C}}}=\text{OR}_{18}$

and/or $-\overset{\text{A}_1}{\underset{\text{H}}{\text{C}}}=\text{N}(\text{R}_{18})_2$ or Z_1 is C_2 - C_{24} alkyl which is interrupted once or more than once by O, S

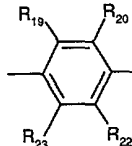
or NR_{14} and which can be substituted by OR_{15} , SR_{15} , $N(R_{16})(R_{17})$, phenyl, halogen, $-\overset{\text{O}}{\underset{\text{H}}{\text{C}}}-\text{CH}_2$,

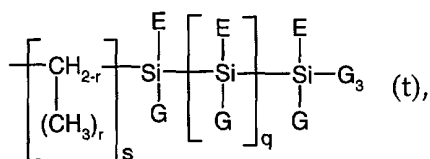
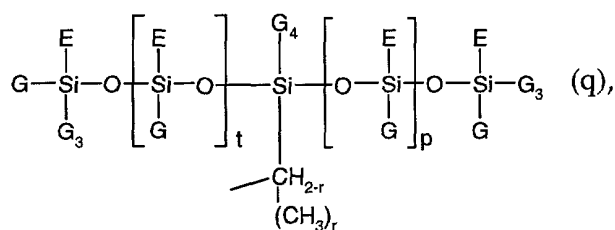
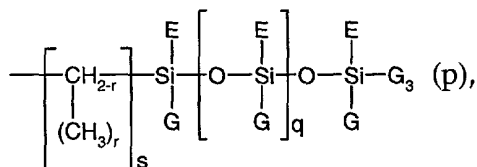
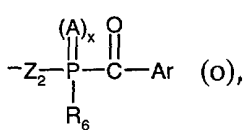
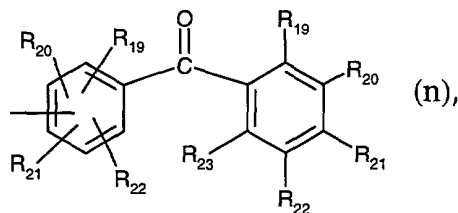
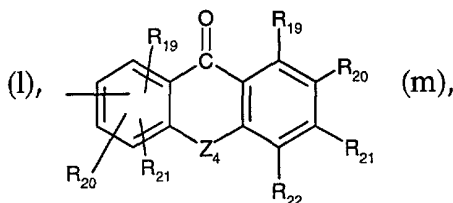
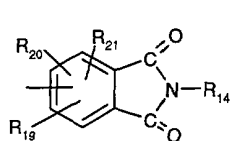
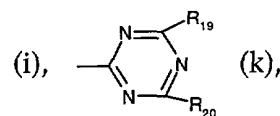
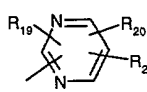
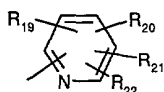
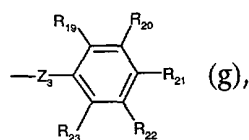
$\text{---}\overset{\overset{\text{A}}{\parallel}}{\text{C}}\text{---R}_{18}$, $\text{---}\overset{\overset{\text{A}}{\parallel}}{\text{C}}\text{---OR}_{18}$ and/or $\text{---}\overset{\overset{\text{A}}{\parallel}}{\text{C}}\text{---N(R}_{18})_2$; or Z₁ is C₁-C₂₄alkoxy, which is substituted once

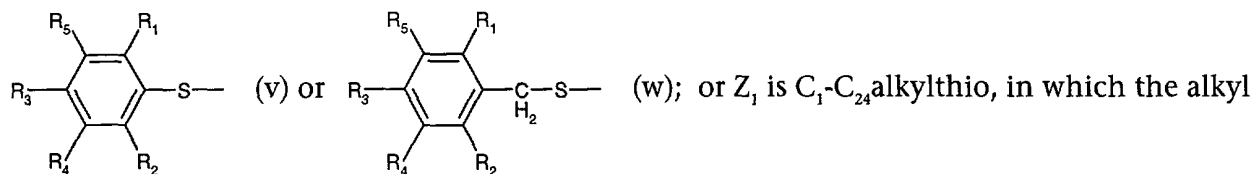
or more than once by phenyl, CN, -N=C=A, $\text{---}\overset{\overset{\text{O}}{\parallel}}{\text{C}}\text{---CH}_2$, $\text{---}\overset{\overset{\text{A}}{\parallel}}{\text{C}}\text{---R}_{18}$, $\text{---}\overset{\overset{\text{A}}{\parallel}}{\text{C}}\text{---OR}_{18}$ and/or

$\text{---}\overset{\overset{\text{A}}{\parallel}}{\text{C}}\text{---N(R}_{18})_2$; or Z₁ is $\text{---}\overset{\overset{\text{A}}{\parallel}}{\text{C}}\text{---OR}_{11}$, $\text{---}\overset{\overset{\text{A}}{\parallel}}{\text{C}}\text{---N(R}_{16})(\text{R}_{17})$, $\text{---}\overset{\overset{\text{A}}{\parallel}}{\text{C}}\text{---OR}_{11a}$ or $\text{---}\overset{\overset{\text{A}}{\parallel}}{\text{C}}\text{---N(R}_{18a})(\text{R}_{18b})$; or

Z₁ is unsubstituted C₃-C₂₄cycloalkyl or C₃-C₂₄cycloalkyl substituted by C₁-C₂₀alkyl, OR₁₁, CF₃ or halogen; unsubstituted C₂-C₂₄alkenyl or C₂-C₂₄alkenyl substituted by C₆-C₁₂aryl, CN, (CO)OR₁₅ or

(CO)N(R₁₈)₂; or Z₁ is C₃-C₂₄cycloalkenyl or is one of the radicals  (f),



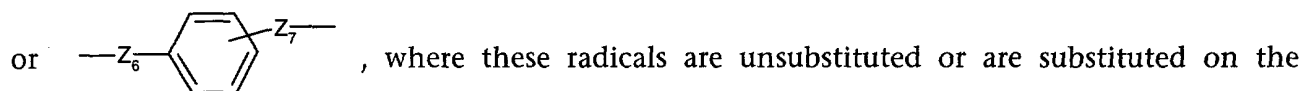
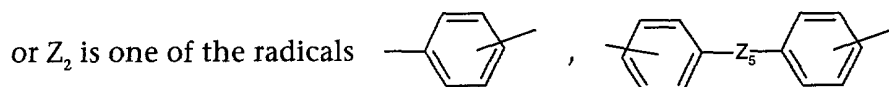


radical is uninterrupted or interrupted once or more than once by nonconsecutive O or S, and is unsubstituted or substituted by OR_{15} , SR_{15} and/or halogen; with the proviso that Z_1 and R_6 are not identical;

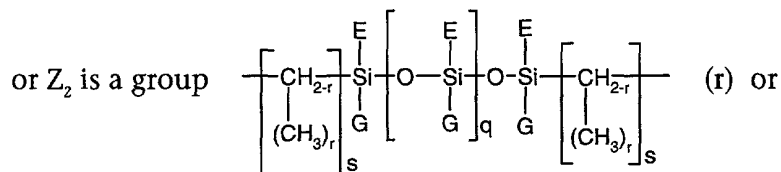
A_1 is O, S or NR_{18a} ;

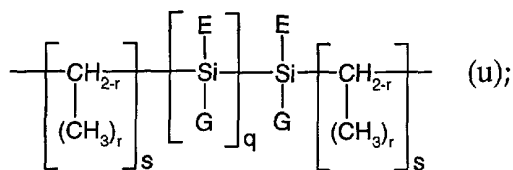
Z_2 is $C_1\text{-}C_{24}$ alkylene; $C_2\text{-}C_{24}$ alkylene interrupted once or more than once by O, S or NR_{14} ; $C_2\text{-}C_{24}$ alkenylene; $C_2\text{-}C_{24}$ alkenylene interrupted once or more than once by O, S or NR_{14} ; $C_3\text{-}C_{24}$ cycloalkylene; $C_3\text{-}C_{24}$ cycloalkylene interrupted once or more than once by O, S or NR_{14} ; $C_3\text{-}C_{24}$ cycloalkylene; $C_3\text{-}C_{24}$ cycloalkenylene interrupted once or more than once by O, S or NR_{14} ;

where the radicals $C_1\text{-}C_{24}$ alkylene, $C_2\text{-}C_{24}$ alkylene, $C_2\text{-}C_{24}$ alkenylene, $C_3\text{-}C_{24}$ cycloalkylene and $C_3\text{-}C_{24}$ cycloalkenylene are unsubstituted or are substituted by $OR_{11'}$, $SR_{11'}$, $N(R_{12})(R_{13})$ and/or halogen;



aromatic by $C_1\text{-}C_{20}$ alkyl; $C_2\text{-}C_{20}$ alkyl which is interrupted once or more than once by nonconsecutive O atoms and which is unsubstituted or substituted by OH and/or SH; $OR_{11'}$, $SR_{11'}$, $N(R_{12})(R_{13})$, phenyl, halogen, NO_2 , CN, $(CO)\text{-}OR_{11'}$, $(CO)\text{-}R_{11'}$, $(CO)\text{-}N(R_{12})(R_{13})$, $SO_2R_{24'}$, $OSO_2R_{24'}$, CF_3 and/or CCl_3 ;





Z_3 is CH_2 , $\text{CH}(\text{OH})$, $\text{CH}(\text{CH}_3)$ or $\text{C}(\text{CH}_3)_2$;

Z_4 is S, O, CH_2 , $\text{C}=\text{O}$, NR_{14} or a direct bond;

Z_5 is S, O, CH_2 , CHCH_3 , $\text{C}(\text{CH}_3)_2$, $\text{C}(\text{CF}_3)_2$, SO , SO_2 , CO ;

Z_6 and Z_7 independently of one another are CH_2 , CHCH_3 or $\text{C}(\text{CH}_3)_2$;

r is 0, 1 or 2;

s is a number from 1 to 12;

q is a number from 0 to 50;

t and p are each a number from 0 to 20;

E , G , G_3 and G_4 independently of one another are unsubstituted C_1 - C_{12} alkyl or C_1 - C_{12} alkyl substituted by halogen, or are unsubstituted phenyl or phenyl substituted by one or more C_1 - C_4 alkyl; or are C_2 - C_{12} alkenyl;

R_{11a} is C_1 - C_{20} alkyl substituted once or more than once by OR_{15} or $-\overset{\text{O}}{\underset{\text{H}}{\text{C}}}-\text{CH}_2$; or is C_2 - C_{20} alkyl

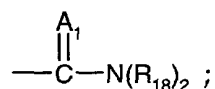
which is interrupted once or more than once by nonconsecutive O atoms and is unsubstituted

or substituted once or more than once by OR_{15} , halogen or $-\overset{\text{O}}{\underset{\text{H}}{\text{C}}}-\text{CH}_2$; or R_{11a} is C_2 - C_{20} alkenyl, C_3 -

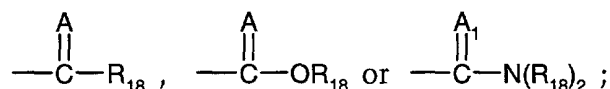
C_{12} alkynyl; or R_{11a} is C_3 - C_{12} cycloalkenyl which is substituted once or more than once by halogen, NO_2 , C_1 - C_6 alkyl, OR_{11} or $\text{C}(\text{O})\text{OR}_{18}$; or C_7 - C_{16} arylalkyl or C_8 - C_{16} arylcycloalkyl;

R_{14} is hydrogen, phenyl, C_1 - C_{12} alkoxy, C_1 - C_{12} alkyl or C_2 - C_{12} alkyl which is interrupted once or more than once by O or S and which is unsubstituted or substituted by OH and/or SH;

R_{15} has one of the meanings given for R_{11} or is a radical $-\overset{\text{A}}{\underset{\text{H}}{\text{C}}}-\text{R}_{18}$, $-\overset{\text{A}}{\underset{\text{H}}{\text{C}}}-\text{OR}_{18}$ or



R_{16} and R_{17} independently of one another have one of the meanings given for R_{12} or are a radical



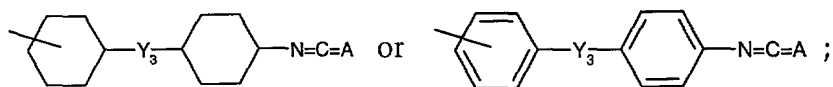
R_{18} is hydrogen, C_1 - C_{24} alkyl, C_2 - C_{12} alkenyl, C_3 - C_8 cycloalkyl, phenyl, benzyl; C_2 - C_{20} alkyl which is interrupted once or more than once by O or S and which is unsubstituted or substituted by OH; R_{18a} and R_{18b} independently of one another are hydrogen; C_1 - C_{20} alkyl, which is substituted once

or more than once by OR_{15} , halogen, styryl, methylstyryl, $-N=C=A$ or $-\overset{\text{O}}{\underset{\text{H}}{\text{C}}}-CH_2$; or C_2 - C_{20} alkyl,

which is interrupted once or more than once by nonconsecutive O atoms and which is unsubstituted or substituted once or more than once by OR_{15} , halogen, styryl, methylstyryl or

$-\overset{\text{O}}{\underset{\text{H}}{\text{C}}}-CH_2$; or R_{18a} and R_{18b} are C_2 - C_{12} alkenyl; C_5 - C_{12} cycloalkyl, which is substituted by $-N=C=A$ or -

$CH_2-N=C=A$ and is additionally unsubstituted or substituted by one or more C_1 - C_4 alkyl; or R_{18a} and R_{18b} are C_6 - C_{12} aryl, unsubstituted or substituted once or more than once by halogen, NO_2 , C_1 - C_6 alkyl, C_2 - C_4 alkenyl, OR_{11} , $-N=C=A$, $-CH_2-N=C=A$ or $C(O)OR_{18}$; or R_{18a} and R_{18b} are C_7 - C_{16} arylalkyl; or R_{18a} and R_{18b} together are C_8 - C_{16} arylcycloalkyl; or R_{18a} and R_{18b} independently of one another are



Y_3 is O, S, SO, SO_2 , CH_2 , $C(CH_3)_2$, $CHCH_3$, $C(CF_3)_2$, (CO), or a direct bond;

R_{19} , R_{20} , R_{21} , R_{22} and R_{23} independently of one another are hydrogen, C_1 - C_{20} alkyl; C_2 - C_{20} alkyl, which is interrupted once or more than once by nonconsecutive O atoms and which is unsubstituted or substituted by OH and/or SH; or R_{19} , R_{20} , R_{21} , R_{22} and R_{23} are OR_{11} , SR_{11} , $N(R_{12})(R_{13})$, NO_2 , CN, SO_2R_{24} , OSO_2R_{24} , CF_3 , CCl_3 , halogen; or phenyl which is unsubstituted or substituted once or more than once by C_1 - C_4 alkyl or C_1 - C_4 alkoxy;

or in each case two of the radicals R_{19} , R_{20} , R_{21} , R_{22} and R_{23} together form C_1 - C_{20} alkylene which is uninterrupted or interrupted by O, S or $-NR_{14}$;

R_{24} is C_1 - C_{12} alkyl, halogen-substituted C_1 - C_{12} alkyl, phenyl, or phenyl substituted by OR_{11} and/or SR_{11} ;

with the proviso that R_6 and Z_1 are not identical,

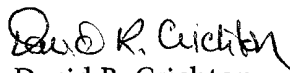
as photoinitiator.

Remarks

Upon entry of the instant Preliminary Amendment, claims 1-18 are pending. Claim 6 has been converted from a "use" claim to a more conventional process format. Claim 12 has been amended to provide reference or subject matter for formulae II and III. The amendments are primarily a matter of form. No new matter has been added.

In view of the foregoing amendments, Applicants aver that the instant claims are now in better condition for examination on the merits. Early favorable action is respectfully solicited. If minor amendments will further prosecution, Applicants request that the Examiner contact the undersigned representative.

Respectfully submitted


David R. Crichton
Attorney for Applicants
Reg. No. 37,300

Ciba Specialty Chemicals Corporation
540 White Plains Road
P.O. Box 2005
Tarrytown, New York 10591-9005
Tel: 914-785-7124
Fax: 914-785-7102
DRC/

MAY 31 2001

APPENDIX - MARKED UP CLAIMS

6. (amended) A method ~~The use of compounds of the formula I as starting materials for the~~ preparation of mono- or bisacylphosphines, mono- or bisacylphosphine oxides or mono- or bisacylphosphine sulfides comprising reacting a compound of formula I according to claim 1.

12. (amended) A photocurable composition comprising

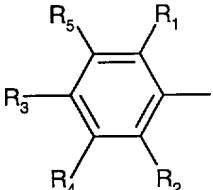
(a) at least one ethylenically unsaturated photopolymerizable compound and

(b) at least one compound of the formula II according to claim 2 or at least one compound

according to formula III
$$\text{Ar}-\overset{\text{O}}{\parallel}{\text{C}}-\overset{\text{(A)}_x}{\underset{\text{R}_6}{\parallel}{\text{P}}}-\text{Z}_1 \quad \text{(III), in which}$$

A is O or S;

x is 0 or 1;

Ar is a group ; or Ar is cyclopentyl, cyclohexyl, naphthyl, anthracyl,

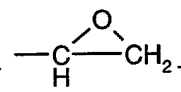
biphenyl or an O-, S- or N-containing 5- or 6-membered heterocyclic ring, where the radicals cyclopentyl, cyclohexyl, naphthyl, anthracyl, biphenyl and 5- or 6-membered heterocyclic ring are unsubstituted or substituted by halogen, C₁-C₄alkyl and/or C₁-C₄alkoxy;

R₁ and R₂ independently of one another are C₁-C₂₀alkyl, OR₁₁, CF₃ or halogen;

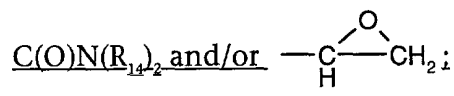
R₃, R₄ and R₅ independently of one another are hydrogen, C₁-C₂₀alkyl, OR₁₁ or halogen;

or in each case two of the radicals R₁, R₂, R₃, R₄ and R₅ together form C₁-C₂₀alkylene which can be interrupted by O, S or -NR₁₄;

R₆ is C₁-C₂₄alkyl, unsubstituted or substituted by C₅-C₂₄cycloalkenyl, phenyl, CN, C(O)R₁₁, C(O)OR₁₁, C(O)N(R₁₄)₂, OC(O)R₁₁, OC(O)OR₁₁, N(R₁₄)C(O)N(R₁₄), OC(O)NR₁₄, N(R₁₄)C(O)OR₁₁,

cycloalkyl, halogen, OR₁₁, SR₁₁, N(R₁₂)(R₁₃) or 

C₂-C₂₄alkyl which is interrupted once or more than once by nonconsecutive O, S or NR₁₄ and which is unsubstituted or substituted by phenyl, OR₁₁, SR₁₁, N(R₁₂)(R₁₃), CN, C(O)R₁₁, C(O)OR₁₁,



C₂-C₂₄alkenyl which is uninterrupted or interrupted once or more than once by nonconsecutive O, S or NR₁₄ and which is unsubstituted or substituted by OR₁₁, SR₁₁ or N(R₁₂)(R₁₃);

C₃-C₂₄cycloalkenyl which is uninterrupted or interrupted once or more than once by nonconsecutive O, S or NR₁₄ and which is unsubstituted or substituted by OR₁₁, SR₁₁ or N(R₁₂)(R₁₃);

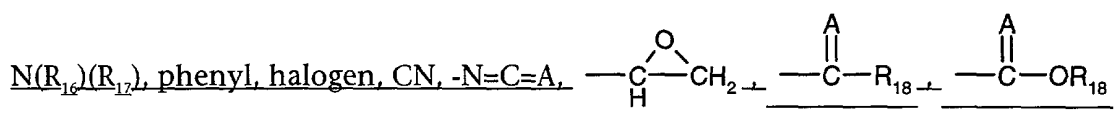
C₇-C₂₄arylalkyl which is unsubstituted or substituted on the aryl group by C₁-C₁₂alkyl, C₁-C₁₂alkoxy or halogen;

C₄-C₂₄cycloalkyl which is uninterrupted or interrupted once or more than once by O, S and/or NR₁₄ and which is unsubstituted or substituted by OR₁₁, SR₁₁ or N(R₁₂)(R₁₃); or C₃-C₂₄arylalkyl or C₃-C₂₄arylalkenyl;

R₁₁ is H, C₁-C₂₀alkyl, C₂-C₂₀alkenyl, C₃-C₈cycloalkyl, phenyl, benzyl or C₂-C₂₀alkyl which is interrupted once or more than once by nonconsecutive O atoms and which is unsubstituted or substituted by OH and/or SH;

R₁₂ and R₁₃ independently of one another are hydrogen, C₁-C₂₀alkyl, C₃-C₈cycloalkyl, phenyl, benzyl or C₂-C₂₀alkyl, which is interrupted once or more than once by O or S and which is unsubstituted or substituted by OH and/or SH; or R₁₂ and R₁₃ together are C₃-C₅alkylene which is uninterrupted or interrupted by O, S or NR₁₄;

Z₁ is C₁-C₂₄alkyl, which is unsubstituted or substituted once or more than once by OR₁₅, SR₁₅,



and/or $\text{---}\overset{\text{A}_1}{\underset{\text{||}}{\text{C}}}\text{---N(R}_{18}\text{)}_2$ or Z₁ is C₂-C₂₄alkyl which is interrupted once or more than once by O, S

or NR₁₄ and which can be substituted by OR₁₅, SR₁₅, N(R₁₆)(R₁₇), phenyl, halogen, $\text{---}\underset{\text{H}}{\overset{\text{O}}{\text{C}}}\text{---CH}_2\text{---}$

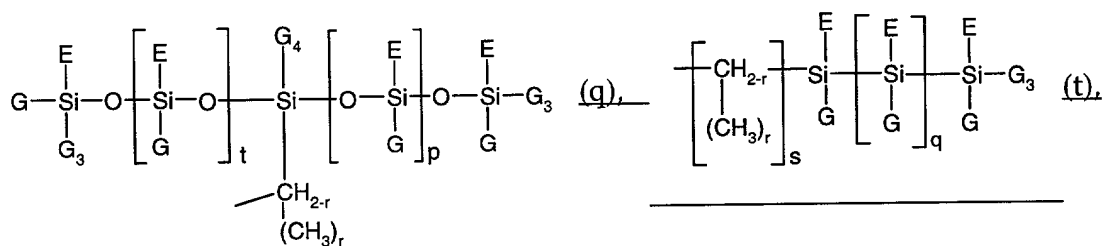
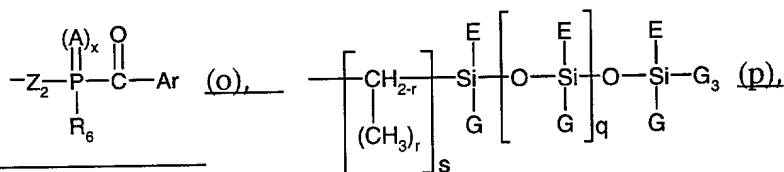
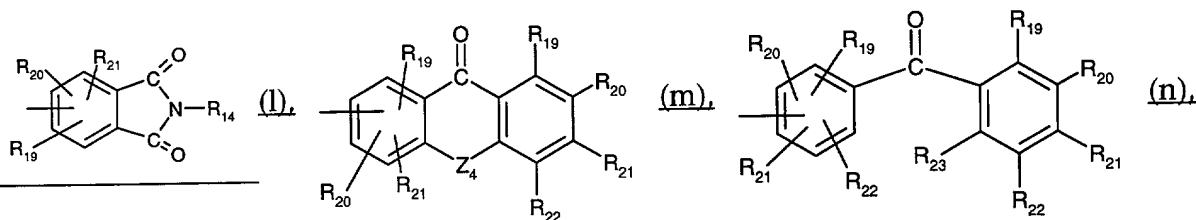
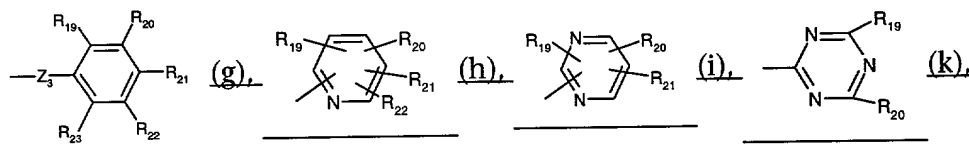
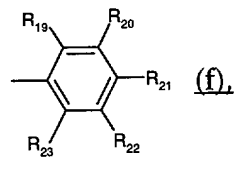
$\text{---}\overset{\text{A}}{\underset{\text{||}}{\text{C}}}\text{---R}_{18}\text{---}$, $\text{---}\overset{\text{A}}{\underset{\text{||}}{\text{C}}}\text{---OR}_{18}$ and/or $\text{---}\overset{\text{A}_1}{\underset{\text{||}}{\text{C}}}\text{---N(R}_{18}\text{)}_2$; or Z₁ is C₁-C₂₄alkoxy, which is substituted once

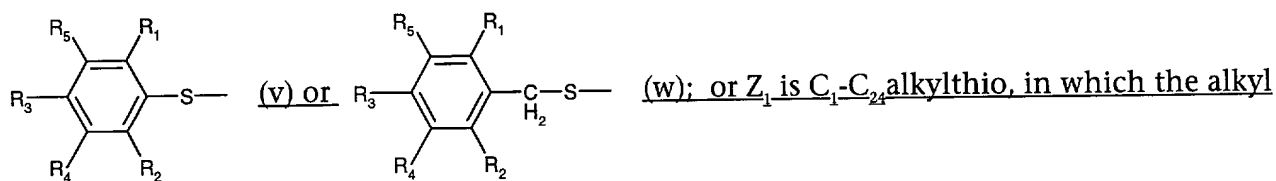
or more than once by phenyl, CN, $-N=C=A$, $-\underset{\text{H}}{\underset{|}{\text{C}}}-\text{O}-\text{CH}_2-$, $-\overset{\text{A}}{\underset{|}{\text{C}}}-\text{R}_{18}-$, $-\overset{\text{A}}{\underset{|}{\text{C}}}-\text{OR}_{18}$ and/or

$-\overset{\text{A}_1}{\underset{|}{\text{C}}}-\text{N}(\text{R}_{18})_2$; or Z_1 is $-\overset{\text{A}}{\underset{|}{\text{C}}}-\text{OR}_{11}-$, $-\overset{\text{A}_1}{\underset{|}{\text{C}}}-\text{N}(\text{R}_{16})(\text{R}_{17})-$, $-\overset{\text{A}}{\underset{|}{\text{C}}}-\text{OR}_{11a}$ or $-\overset{\text{A}_1}{\underset{|}{\text{C}}}-\text{N}(\text{R}_{18a})(\text{R}_{18b})$; or

Z_1 is unsubstituted C_3-C_{24} cycloalkyl or C_3-C_{24} cycloalkyl substituted by C_1-C_{20} alkyl, OR_{11} , CF_3 or halogen; unsubstituted C_2-C_{24} alkenyl or C_2-C_{24} alkenyl substituted by C_6-C_{12} aryl, CN, $(\text{CO})\text{OR}_{15}$ or

$(\text{CO})\text{N}(\text{R}_{18})_2$; or Z_1 is C_2-C_{24} cycloalkenyl or is one of the radicals



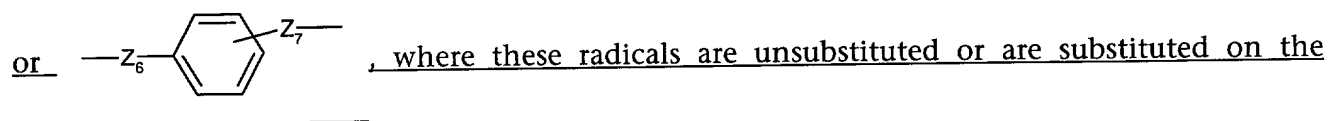
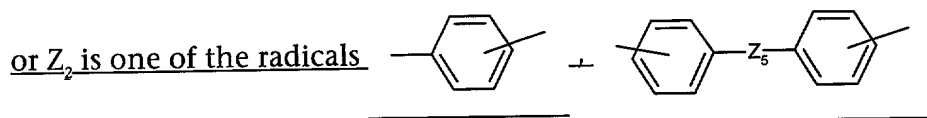


radical is uninterrupted or interrupted once or more than once by nonconsecutive O or S, and is unsubstituted or substituted by OR_{15} , SR_{15} and/or halogen; with the proviso that Z_1 and R_6 are not identical;

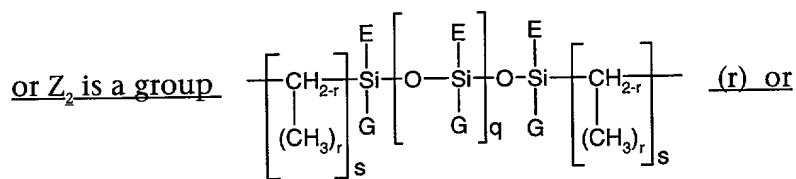
A_1 is O, S or NR_{18a} ;

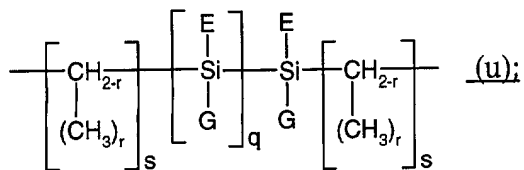
Z_2 is $C_1\text{-}C_{24}$ alkylene; $C_2\text{-}C_{24}$ alkylene interrupted once or more than once by O, S or NR_{14} ; $C_2\text{-}C_{24}$ alkenylene; $C_2\text{-}C_{24}$ alkenylene interrupted once or more than once by O, S or NR_{14} ; $C_3\text{-}C_{24}$ cycloalkylene; $C_3\text{-}C_{24}$ cycloalkylene interrupted once or more than once by O, S or NR_{14} ; $C_3\text{-}C_{24}$ cycloalkenylene; $C_3\text{-}C_{24}$ cycloalkenylene interrupted once or more than once by O, S or NR_{14} ;

where the radicals $C_1\text{-}C_{24}$ alkylene, $C_2\text{-}C_{24}$ alkylene, $C_2\text{-}C_{24}$ alkenylene, $C_3\text{-}C_{24}$ cycloalkylene and $C_3\text{-}C_{24}$ cycloalkenylene are unsubstituted or are substituted by OR_{11} , SR_{11} , $N(R_{12})(R_{13})$ and/or halogen;



aromatic by $C_1\text{-}C_{20}$ alkyl; $C_2\text{-}C_{20}$ alkyl which is interrupted once or more than once by nonconsecutive O atoms and which is unsubstituted or substituted by OH and/or SH; OR_{11} , SR_{11} , $N(R_{12})(R_{13})$, phenyl, halogen, NO_2 , CN, $(CO)\text{-}OR_{11}$, $(CO)\text{-}R_{11}$, $(CO)\text{-}N(R_{12})(R_{13})$, SO_2R_{24} , OSO_2R_{24} , CF_3 and/or CCl_3 ;





Z₃ is CH₂, CH(OH), CH(CH₃) or C(CH₃)₂;

Z₄ is S, O, CH₂, C=O, NR₁₄ or a direct bond;

Z₅ is S, O, CH₂, CHCH₃, C(CH₃)₂, C(CF₃)₂, SO, SO₂, CO;

Z₆ and Z₇ independently of one another are CH₂, CHCH₃ or C(CH₃)₂;

r is 0, 1 or 2;

s is a number from 1 to 12;

q is a number from 0 to 50;

t and p are each a number from 0 to 20;

E, G, G₃ and G₄ independently of one another are unsubstituted C₁-C₁₂alkyl or C₁-C₁₂alkyl substituted by halogen, or are unsubstituted phenyl or phenyl substituted by one or more C₁-C₄alkyl; or are C₂-C₁₂alkenyl;

R_{11a} is C₁-C₂₀alkyl substituted once or more than once by OR₁₅ or $\begin{array}{c} \text{O} \\ | \\ -\text{C}-\text{CH}_2 \\ | \\ \text{H} \end{array}$; or is C₂-C₂₀alkyl

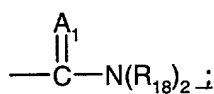
which is interrupted once or more than once by nonconsecutive O atoms and is unsubstituted

or substituted once or more than once by OR₁₅, halogen or $\begin{array}{c} \text{O} \\ | \\ -\text{C}-\text{CH}_2 \\ | \\ \text{H} \end{array}$; or R_{11a} is C₂-C₂₀alkenyl, C₃-

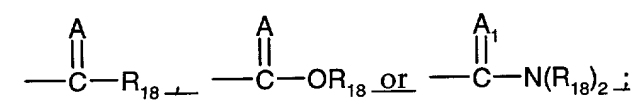
C₁₂alkynyl; or R_{11a} is C₃-C₁₂cycloalkenyl which is substituted once or more than once by halogen, NO₂, C₁-C₆alkyl, OR₁₁ or C(O)OR₁₈; or C₇-C₁₆arylalkyl or C₈-C₁₆arylcycloalkyl;

R₁₄ is hydrogen, phenyl, C₁-C₁₂alkoxy, C₁-C₁₂alkyl or C₂-C₁₂alkyl which is interrupted once or more than once by O or S and which is unsubstituted or substituted by OH and/or SH;

R₁₅ has one of the meanings given for R₁₁ or is a radical $\begin{array}{c} \text{A} \\ || \\ -\text{C}-\text{R}_{18} \end{array}$ or $\begin{array}{c} \text{A} \\ || \\ -\text{C}-\text{OR}_{18} \end{array}$ or



R₁₆ and R₁₇ independently of one another have one of the meanings given for R₁₂ or are a radical



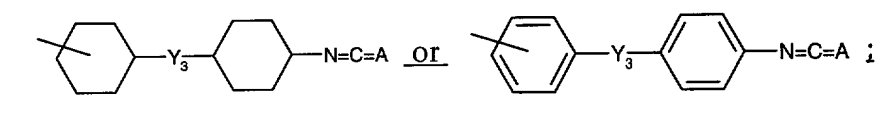
R₁₈ is hydrogen, C₁-C₂₄alkyl, C₂-C₁₂alkenyl, C₃-C₈cycloalkyl, phenyl, benzyl; C₂-C₂₀alkyl which is interrupted once or more than once by O or S and which is unsubstituted or substituted by OH;

R_{18a} and R_{18b} independently of one another are hydrogen; C₁-C₂₀alkyl, which is substituted once or more than once by OR₁₅, halogen, styryl, methylstyryl, -N=C=A or $\text{---}\overset{\overset{\text{O}}{\parallel}}{\text{C}}\text{---CH}_2$; or C₂-C₂₀alkyl,

which is interrupted once or more than once by nonconsecutive O atoms and which is unsubstituted or substituted once or more than once by OR₁₅, halogen, styryl, methylstyryl or

$\text{---}\overset{\overset{\text{O}}{\parallel}}{\text{C}}\text{---CH}_2$; or R_{18a} and R_{18b} are C₂-C₁₂alkenyl; C₅-C₁₂cycloalkyl, which is substituted by -N=C=A or -

CH₂-N=C=A and is additionally unsubstituted or substituted by one or more C₁-C₄alkyl; or R_{18a} and R_{18b} are C₆-C₁₂aryl, unsubstituted or substituted once or more than once by halogen, NO₂, C₁-C₆alkyl, C₂-C₄alkenyl, OR₁₁, -N=C=A, -CH₂-N=C=A or C(O)OR₁₈; or R_{18a} and R_{18b} are C₇-C₁₆arylalkyl; or R_{18a} and R_{18b} together are C₈-C₁₆arylcycloalkyl; or R_{18a} and R_{18b} independently of one another are



Y₃ is O, S, SO, SO₂, CH₂, C(CH₃)₂, CHCH₃, C(CF₃)₂, (CO), or a direct bond;

R₁₉, R₂₀, R₂₁, R₂₂ and R₂₃ independently of one another are hydrogen, C₁-C₂₀alkyl; C₂-C₂₀alkyl, which is interrupted once or more than once by nonconsecutive O atoms and which is unsubstituted or substituted by OH and/or SH; or R₁₉, R₂₀, R₂₁, R₂₂ and R₂₃ are OR₁₁, SR₁₁, N(R₁₂)(R₁₃), NO₂, CN, SO₂R₂₄, OSO₂R₂₄, CF₃, CCl₃, halogen; or phenyl which is unsubstituted or substituted once or more than once by C₁-C₄alkyl or C₁-C₄alkoxy;

or in each case two of the radicals R₁₉, R₂₀, R₂₁, R₂₂ and R₂₃ together form C₁-C₂₀alkylene which is uninterrupted or interrupted by O, S or -NR₁₄;

R₂₄ is C₁-C₁₂alkyl, halogen-substituted C₁-C₁₂alkyl, phenyl, or phenyl substituted by OR₁₁ and/or SR₁₁;

with the proviso that R₆ and Z₁ are not identical.

1. *Chlorophyll a* (Chl *a*)